CHEMICALLY FRACTIONATED FISSION (CFF) XE IN OKELOBONDO (ZONE 13 OF OKLO): IMPLICATIONS FOR THE ORIGIN OF TERRESTRIAL XENON, A. Meshik[1], C. Hohenberg[1], K. Kehm[1], P. Swan[1], and Yu. Dymkov[2]; [1]Washington Univ., Dept. of Physics, St. Louis, MO 63130; [2]Union Institute of Chemical Technology, Kashirskoe 33, Moscow.

There is no final answer for the question: why terrestrial Xe is unique in the Solar system. It has been suggested that primary terrestrial Xe is derived from solar Xe by severe isotopic mass-fractionation during hydrodynamic loss of the primitive atmosphere [1], or as a result of a giant meteoritic impact [2], or as a consequence of gravitational fractionation in a porous planetesimal material [3]. In many of these models hypothetical U-Xe is needed with solar Xe, which must be then fractionated and combined with ^{244}Pu and/or ^{238}U fission Xe to produce modern atmospheric Xe. If so, then a question arises: Why have terrestrial Xe and Kr fractionated in different directions, and why was Ar not fractionated at all? U-Xe is required as a fundamental component but there is no direct experimental evidence for its existence. These difficulties were the main motivation for this work; we suggest here an alternative approach to understanding the composition of terrestrial Xe.
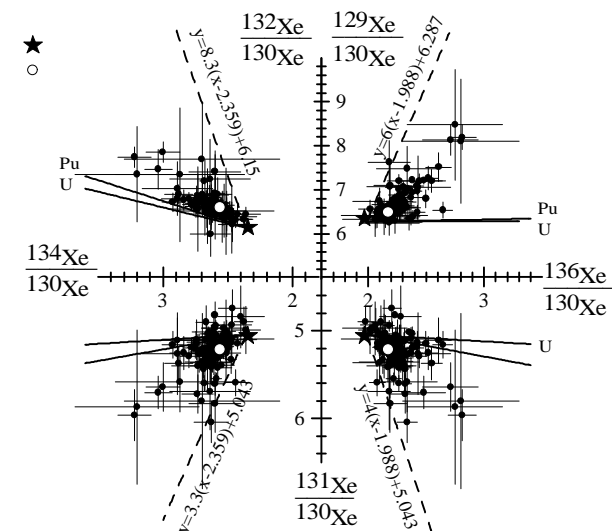

Fig. 1. Points comprise available published terrestrial values in various geological environments [4–16]. Also shown are directions to Xe components derived from fission of ^{238}U, ^{244}Pu, and to some "new" end member (dash lines and their equations).

The observed variations in Xe isotopic compositions (excluding ^{129}Xe) in various terrestrial materials (Fig. 1) can not be explained by simple (or fractionated) mixtures of atmospheric, planetary (AVCC) Xe and fissiogenic Xe. Let us suppose that these variations are due to the admixture of some "new" component and, on the basis of available data, explore whether a single new component is sufficient to constrain its isotopic structure. The sufficiency of a single new component can be shown graphically. If we draw the "end member" lines on Fig. 1 and calculate their slopes, one can derive the required isotopic composition of this component. Of course, this composition is not necessarily the true end member since new data may change the result, but it

does suggest an isotopic structure which, when added to known components, reproduces the known suite of terrestrial samples. The inferred composition is: ^{136}Xe : ^{134}Xe : ^{132}Xe : ^{131}Xe : ^{130}Xe : ^{129}Xe = 1 : 1.2 : 10 : 4 : 6 (plotted at Fig. 3a). There are no known heavy nuclei whose fission can produce this isotopic pattern, nor can other simple nuclear reactions. However, if we compare this isotopic composition with Xe derived from ^{238}U spontaneous fission we find a good correlation with the time constants for stable Xe production from the decay chains of the corresponding precursors (Fig 2). This behavior suggests that such a component is real, not just the hypothetical end member, and it is the result of chemically selective migration of the Xe and Kr precursors.
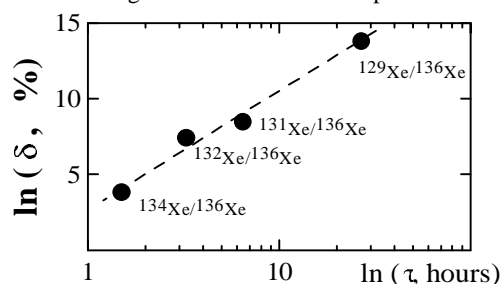

Fig. 2. Correlation between relative isotope excesses (δ) of "new" component comparing with Xe from ^{238}U fission and life times (τ) of β-active precursors of Xe.
$$\xi = [(^A Xe/^{136}Xe)/(^A Xe/^{136}Xe)_{238U} - 1] \times 100\%$$

According to this hypothesis the observed anomalies are due to the fast diffusion of fission fragments (Sn, Sb, Te, I, Se, and Br) from the parent U-bearing mineral into the adjacent phases where they subsequently decay into stable Xe and Kr isotopes. This results in a new pseudo-component whose isotopic composition is determined by the lifetime and the hot-atom chemistry of the recoiling fragment. We refer to this component as CFF, an abbreviation for _C_hemically _F_ractionated _F_ission. If the CFF-Xe is indeed a significant contributor to the earth's atmosphere, it must be present in sufficient abundance somewhere in the solid earth. There are some indications (for example, Fig. 3b, c) but most of these materials could hardly be a quantitative source of atmospheric CFF-Xe. More probably this source is due to early neutron-induced fission of ^{235}U in U-rich ores. For this reason we were especially interested in the natural nuclear reactor: the Oklo uranium mine. The initial Xe isotopic study of Oklo [18] left no doubt that a natural nuclear reactor had indeed been there: Xe released from the ore had the isotopic pattern of ^{235}U neutron induced fission, with a small contribution from ^{239}Pu neutron induced fission. Later isotopically anomalous Xe, enriched mainly in ^{132}Xe and ^{131}Xe, was identified in zone Z-2, but its origin was attributed to the fission of an superheavy element [19, 20]. Similar anomalies were later found in zone Z-3 and it was proved that overabundances of ^{132}Xe, ^{131}Xe, ^{129}Xe and ^{134}Xe were due to the migration of Xe radioactive precursors [20, 21].

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However, in these earlier studies, the dominant Xe contribution was still from ^{235}U neutron-induced fission, with the fraction of anomalous CFF-Xe never exceeding a few percent. Therefore this work was undertaken to find a sample where CFF-Xe is the most abundant component. Finding it in high concentrations allows us to study the isotopic structures of this new xenon component and pursue implications of its existence as a new heavy noble gas component in nature.
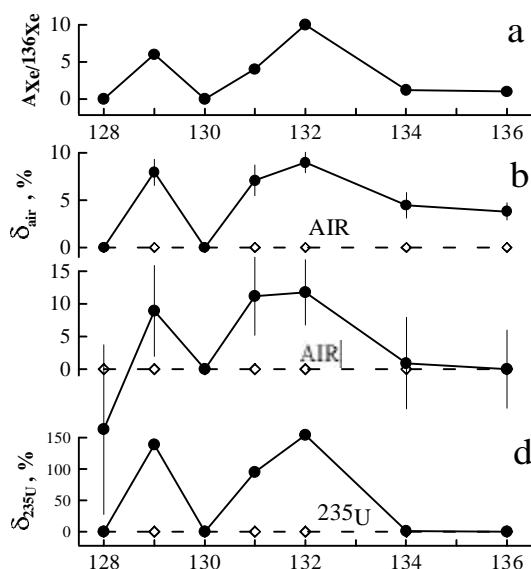

Fig. 3. Isotopic composition of CFF-Xe in terrestrial atmosphere calculated from slopes of end member lines – (a), and isotopic excesses (relative to air) in Greenland anorthosite [17] – (b), in CH31-DR11-NG glass from MORB [12] – (c), and in Oklelobondo [this work] – (d).

Since 1972 at least sixteen individual reactors have been discovered in the Oklo mine area, with the first nine reactors (zones 1–9) discovered much earlier, studied in more detail. The "newly" discovered reactors (zones 10 to 16) are located totally underground and have not been subjected to weathering or surface water. One might then expect to find a more pristine record of reactor-produced Kr and Xe in this material than in the previously studied zones of the Oklo deposit.

Using microanalytical laser extraction techniques [23], we analyzed Xe and Kr in a pulse-counting mass spectrometer [24] in various mineral phases of sample from reactor zone 13 from Okelobondo, in the southern extension of the Oklo deposit [25]. The Nd-YAG laser, operating in the Q-switched mode, allows us to selectively extract noble gases from a thick polished section with the spatial resolution of $10\,\mu$m. Typically one 0.3 sec long burst of 25W @ 500 Hz was used to degas about 8 nanograms, typically releasing some $10^{-12} – 10^{-11}$ cc STP of Xe.

Isotopic compositions and concentrations of Xe and Kr vary depending on mineral phase (determined by SEM-EDX). The main phases (U oxides) have mostly neutron-induced Xe. But the U-free inclusions, which consist of an alumophosphate (probably wavellite), have the distinct signa-

ture of CFF-Xe (Fig. 3d). Moreover, this phase has the highest Xe concentrations (more than 10^{-2} cc/g) ever measured in natural materials. Compared with normal Oklo Xe, derived primarily from ^{235}U fission, there are enrichments of 150% in ^{132}Xe and ^{129}Xe, 95% in ^{131}Xe, and 1% in ^{134}Xe. The fact that the anomalous Xe is concentrated in the U-free phase is a strong argument in favor of the CFF-hypothesis. This effect is less pronounced for Kr due to it's lower fission yield and higher level of the local air contamination.

According to our earlier estimation [18], a terrestrial atmospheric Xe content of about 1% of CFF-^{136}Xe is needed to explain its composition, requiring 3×10^{14} cc STP. To provide this amount of CFF-Xe in the atmosphere about 10^{10} tons of the Okelobondo alumophosphare has to be degassed. Although this sounds large, it is not unreasonable on the planetary scale. It implies that only about 1 billionth of total U inventory in the Earth's crust must have gone through an early reactor stage and released its Xe by chemical fractionation. Moreover, there is other evidence for CFF-Xe in common rocks where no nuclear chain reaction has been directly involved (Fig. 1).

To summarize, if one accepts the CFF hypothesis, neither U-Xe nor ad-hoc scenarios to explain Xe and Kr fractionating in different directions are required to explain atmospheric Xe. CFF is a natural pseudo-component that must exist at some level in the terrestrial environment, whether or not it explains the structure of atmospheric Xe.

REFERENCES [1] D. M. Hunten, R. O. Pepin, and J. C. G. Walker, *Icarus* **69** (1987) 532; [2] W. Benz and A. G. W. Cameron, *Origin of the Earth*, (1990) NY, p. 61; [3] M. Ozima and K. Nakasawa, *Nature*, **284** (1980) 313; [4] G. A. Bennett & O. K. Manuel, *GCA*, **34** (1970) 593; [5] W. A. Butler et al, *Journ. Geoph. Res.*, **68** (1963) 3283, [6] M. S. Boulos, & O. K. Manuel, *Science*, 174 (1971) 1334, [7] D. P. Thompson et al., *Phys. Of Earth and Planet Interior*, **17** (1978) 98; [8] I. Kaneoka & N. Takaoka, *EPSL*, **39** (1978) 382; [9] D. Phinney et al., *Journ. Geophys. Res.*, **83** (1978) 2313; [10] Smith & Reynolds, *EPSL*, **54** (1981) 236; [11] Th. Staudacher & C. J. Allegre, *EPSL*, **60** (1982) 389; [12] B. Marty, *EPSL*, **94** (1989) 45; [13] M. Ozima & S. Zashu, *EPSL*, **105** (1991) 13; [14] S. V. S. Murty, *Chem. Geol.*, **94** (1992) 229; [15] H. Hiyagon et al., *GCA*, **56** (1992) 1301; [16] J. Poreda & K. A. Farley, *EPSL*, **113** (1992) 129; [17] P. M. Jefferey, *Nature* **233** (1971) 260; [18] R. J. Drozd, C. M. Hohenberg, and C. J. Morgan, *EPSL*, **23** (1974) 28; 1604; [19] Yu. A. Shukolyukov, et al. *Geokhimiya* **11** (1977); [20] Yu. Shukolyukov, *Fission products of heavy elements on the Earth*, Moscow, Energoizdat, (1982); [21] A. P. Meshik, et al. *Proc. of XI Symosium on Isotope Geochemistry*, Moscow, (1986) 237; [22] A. P. Meshik, Ph.D. theses (1988) Vernadsky Inst., Moscow; [23] R. H. Nichols, Jr, K. Kehm, and C. M. Hohenberg, *Advanced in Analytical Geoche.*, **2** (1995) 119; [24] C. M. Hohenberg, *Rev. Sci. Instr.* **51** (1980) 1075; [25]; This sample was provided by Dr. Maurice Pagel, CREGU, France; [26] A. P. Meshik et al. *Abstr. of Goldschmidt Conerence.* (1996) 400.